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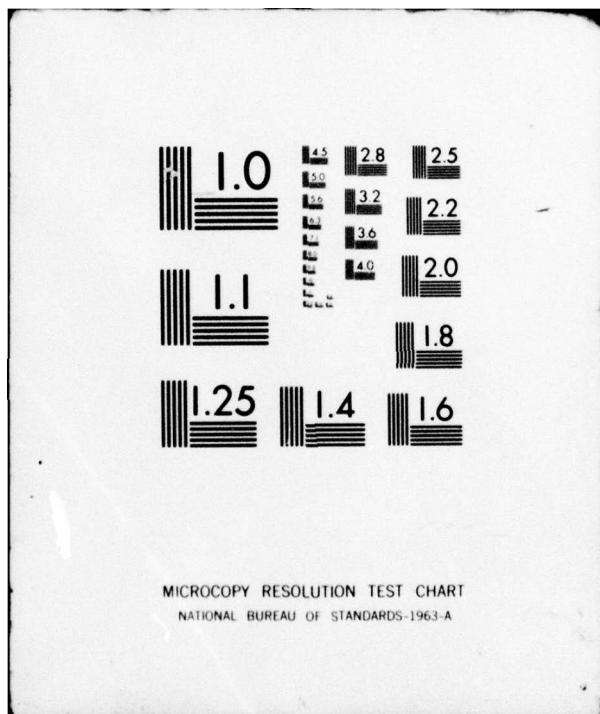
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STRESS CORROSION CRACKING AND HYDROGEN EMBRITTLEMENT:

DIFFERENCES AND SIMILARITIES

by

R.M. Latanision, O.H. Gastine, and C.R. Compeau

Technical Report No. 1

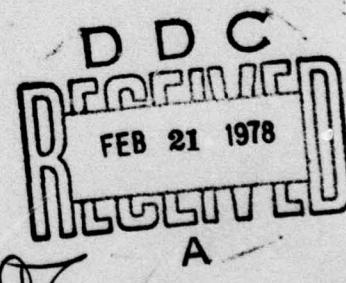
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STRESS CORROSION CRACKING AND HYDROGEN EMBRITTLEMENT:

DIFFERENCES AND SIMILARITIES

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Over the years many criteria have been proposed for distinguishing, phenomenologically at least, stress corrosion cracking from hydrogen embrittlement. At one time, for example, the susceptibility of an alloy to cracking at anodic potentials was considered characteristic of a material sensitive to SCC. Conversely, increased sensitivity at cathodic potentials was considered evidence of HEM. This potential dependence is clearly an uncertain criterion since it is now appreciated that crack tip conditions (potential and pH) may vary considerably from those more easily measured at the bulk metal/electrolyte interface. In this discussion, we will trace the development, and dismissal in some cases, of various criteria for distinguishing SCC from HEM based on, for example, hydrogen-induced phase transformations in the solid, the observation of hydrogen evolution from the tip of a propagating crack, fractography, crystal structure, critical anionic species in the electrolyte, loading mode during deformation, and the influence of solid state impurities.

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1. Introduction

Premature failure of materials such as aluminum alloy 7075 and austenitic stainless steel, for example, occurs in aqueous chloride environments. Whether these failures should be attributed to hydrogen embrittlement (HEM) or to stress corrosion cracking (SCC) is the subject of considerable interest and concern. If it were possible to invoke a universally acceptable criterion to distinguish, at least phenomenologically, between these embrittling phenomena the issue would be resolved. No such criterion of which we are aware exists at the present. What we hope to do in this discussion, however, is to examine those criteria which have been proposed over the years maintaining as a common factor embrittlement in aqueous electrolytes. We will, therefore, not treat embrittlement in a gaseous hydrogen atmosphere except for the purpose of comparison where the need arises.

The implication of the above approach is that stress corrosion cracking and hydrogen embrittlement in electrolytes are truly distinct phenomena-- a point on which agreement is far from universal.¹ There are to be sure many similarities:

- a. A general increase in sensitivity to degradation as the strength of an alloy or family of alloys is increased.
- b. A generally parallel dependence of susceptibility to embrittlement (or perhaps better, to reduction in ductility) on slip mode in the alloy -- alloys which are most sensitive typically exhibit planar slip, which may be due to a relatively low stacking fault energy (SFE), shearing of coherent precipitates, or local ordering in the alloy.²
- c. Discontinuous crack propagation
- d. Similar dependence of crack propagation rates (velocity) on stress intensity -- i.e., the familiar three stage v-K curves^{3,4}.
- e. The existence of a threshold stress (or stress intensity) below which delayed failure or crack propagation are not observed.
- f. Similar grain size dependencies in hydrogen gas and in aqueous environments.
- g. Similarities in response to metallurgical variables in some systems.
- h. Somewhat similar temperature and strain rate dependencies.

These and other correlations have been thoroughly described in a comprehensive review by Thompson and Bernstein². It is not clear to us, however, that a description of such parallelisms is particularly instructive for the present purpose -- namely, to distinguish hydrogen embrittlement from stress corrosion cracking -- although such observations do suggest important fundamental or mechanistic similarities. One might, for example, consider whether any significance should be attached to the observation of similar v-K behavior in an alloy examined for stress corrosion cracking as opposed to one ostensibly examined to determine its hydrogen embrittlement susceptibility, i.e., does this provide a basis for distinguishing phenomena? Perhaps activation energy measurements in stage II may provide a means of distinguishing SEC and HEM. On the other hand, sola-lime glass⁵ and polymers⁶ exhibit similar v-K curves when exposed to aggressive environments, so in many respects v-K curves are generic with regard to embrittlement phenomena.

In any case, it seems to us that the differences in response which have been attributed to HEM on the one hand and SCC on the other are more interesting points for discussion. In this context, there are extremes in behavior which seem clearly attributable to SCC or HEM -- for example, the cracking of α -brass in ammoniacal solutions and the failure of HSLA steels in moist air, respectively. More interesting for our purposes are alloy systems where the distinction is perhaps less perfect -- the austenitic stainless steels in aqueous chlorides and 7000-series aluminum alloys in halide environments, for example, which are the subjects of considerable current controversy.^{1,7-10}.

In the next section we will briefly summarize the models which are in more or less current favor with respect to HEM and SCC and then turn to the specifics of various criteria which have over the years been considered as a means of distinguishing between these two phenomena.

2. The Models of Hydrogen Embrittlement and Stress Corrosion Cracking

Hydrogen embrittlement and stress corrosion cracking have been and will surely continue to be of enormous academic as well as technological interest. In consequence, several international conferences¹¹⁻¹³ have been held and their proceedings contain detailed reviews and critical assessments of the proposed models. We, therefore, at this point wish only to list in summary form short descriptions of views which enjoy some current popularity leaving details to the previously mentioned sources.

2.1 Mechanisms of Stress Corrosion Cracking

The various models of stress corrosion cracking -- premature cracking under the simultaneous action of a generally specific corrosive agent and a tensile stress -- can be largely divided into two basic classes: those which consider that crack propagation proceeds by anodic dissolution at the crack tip (dissolution models) and those which consider that crack propagation is essentially mechanical. Those mechanisms have been summarized in more detail elsewhere^{14,15} but are listed briefly below.

- a. Crack propagation by the dissolution of film-free metal due to an increase in the number of active sites provided by plastic deformation at the crack tip. This mechano-chemical model was proposed by Hoar and Hines¹⁶.
- b. Crack propagation by the dissolution of metal at the crack tip as a consequence of the rupture of otherwise protective surface films by emergent dislocations. The film-rupture or slip step dissolution model has several variations, but is largely similar to that proposed initially by Champion¹⁷ and Logan¹⁸.
- c. Propagation of cracks by the repeated formation and rupture of a brittle film growing into the metal at the crack tip as first described by Forty¹⁹.
- d. Adsorption (stress sorption) of surface active species, the consequence of which is a reduction in the surface energy required to form a crack and, therefore, reduced fracture stress. This adsorption model has been applied to various embrittlement phenomena since its proposal by Petch²⁰ and has been discussed with relation to stress corrosion cracking by Uhlig²¹.

2.2 Mechanisms of Hydrogen Embrittlement

Hydrogen induced losses in strength or ductility (typically expressed in terms of reduction in area) have been attributed to several mechanisms. These have been succinctly described by Louthan and McNitt²² and the list below is essentially that which appeared in their publication.

- a. The accumulation of molecular hydrogen in internal voids and cracks exerts a pressure which lowers the apparent fracture stress. This pressure model was originally proposed by Zapffe²³.
- b. A hydrogen-induced decohesion of the lattice proposed by Troiano²⁴ and modified by Oriani²⁵.
- c. Adsorption (stress sorption) of hydrogen to reduce the surface energy as proposed by Petch, i.e., the hydrogen equivalent of (d) above.
- d. Beachem's²⁶ suggestion that (absorbed) hydrogen-stimulated plastic deformation accelerates subsequent fracture. Though unspecific with regard to the means by which plasticity might be affected, recent field ion microscopy by Clum²⁷ suggests that hydrogen may reduce the work required to nucleate dislocations at the surface and, hence, induces plasticity.
- e. Formation of a hydrogen-rich phase (e.g., hydride) which has mechanical properties different than those of the matrix^{28,29}.
- f. Hydrogen-dislocation interactions which suppress glide and provide a means of producing locally large hydrogen accumulations that induce subsequent embrittlement^{30,31}.

It is not our purpose in this instance to critically assess the above models. This has been done by others^{2,14,15,22} and most counter-arguments are well established. Considering the volume of literature which has appeared on these subjects, it is no surprise that evidence can be found to contradict virtually every point of view. What is emerging, it seems,^{2,7} though hardly unanimously, is that there are incidence of phenomena which appear best understood in terms of some dissolution-related mechanism while others equally clearly involve hydrogen. In between these extremes it seems to us difficult to clearly assess the majority contributor. For example, accelerated dissolution in acids may stimulate the generation of cathodically produced hydrogen on a straining electrode. If premature failure occurs in such cases, is it due to stress corrosion cracking or to hydrogen embrittlement? We will try to provide an indication of attempts to answer this question.

3. Proposed Criteria for Distinguishing Hydrogen Embrittlement from Stress Corrosion Cracking

In the past, several different points of view have emerged with regard to the characteristics of delayed failure phenomena of alloys in electrolytes which might be used as diagnostics. Some of these are no longer popular, but all have shared in developing current opinions. The following discussion of several of these points of view is not intended to be exhaustive, and we acknowledge the likelihood of omissions which others may consider significant. It is hoped that the following may, however, be instructive.

3.1. Active Path Corrosion vs. Hydrogen Embrittlement: The Potential Dependence of Failure Phenomena

Studies of the influence of the electrochemical polarization on the cracking of high strength steels in electrolytes have led to the proposal that two types of mechanisms may operate. These mechanisms -- active path corrosion (APC) and hydrogen embrittlement -- are shown in Figure 1 which is taken from the work of Wilde³². Figure 1(a) schematically shows APC wherein crack propagation is presumed to occur by anodic dissolution along a pre-existing susceptible path in the metal. In this model, Wilde³² points out that the cathodic partial process (proton reduction) serves only as a means of consuming electrons generated by the anodic reaction. Hydrogen embrittlement, Figure 1(b), is principally controlled by production and absorption of atomic hydrogen into the metal at cathodic sites followed by a hydrogen-induced brittle failure. The potential (or current) dependence of the time-to-failure, T_f , may in principle be used to distinguish these phenomena. In Figure 2(B), T_f decreases as cathodic currents are imposed and increases with anodic polarization, presumably evidence of hydrogen embrittlement. The converse is true in Figure 2(C) in which case APC is the proposed cracking mechanism, cathodic protection thereby retarding crack propagation. Combinations such as Figures 2(A) and 2(D) were considered to indicate open circuit cracking according to an APC or hydrogen mechanism, respectively.

Behavior such as that shown schematically in Figure 2(A) has been reported for 12% Cr-martensitic stainless steel in aerated NaCl solutions³³. Although it was initially considered that a dual mechanism thus applied -- i.e., hydrogen embrittlement at cathodic currents and APC at anodic potentials -- Truman³⁴ and later Wilde³² demonstrated convincingly that hydrogen embrittlement was the operative mechanism in both potential regimes. That a single mechanism should operate under both conditions is not surprising considering the fractographic evidence which shows that crack paths in high strength steels at both anodic and cathodic potentials are identical, or at least very similar: a primary intergranular crack following prior austenite grain boundaries and a secondary (shear) transgranular failure associated with a shear lip^{35,36}. The electrochemical basis for the above conclusion is the fact that conditions in a localized geometry may be quite different than in the bulk electrolyte or on a smooth surface. In particular, Brown, et al.³⁷ have shown that the pH measured in the crack tip of a 0.45 C steel exposed to aqueous NaCl was 3.8 regardless of the bulk pH. Hence, even though hydrogen production should not occur at the bulk pH and potential, proton reduction may occur in the crack tip, provided an appropriate potential is also present in the crack tip. Support for this conclusion is found in studies which show hydrogen permeation through pitted steel polarized to potentials noble to the reversible hydrogen potential^{32,38} as well as the observation of hydrogen evolution from pre-cracked cantilever beam specimens in NaCl solutions³⁹. In effect, then, the behavior of high strength steel, typified by Figure 2(A), may be interpreted on a basis consistent with hydrogen embrittlement at all potentials: at active potentials, hydrogen is produced by the bulk discharge of protons whereas at noble potentials the acid hydrolysis of anodic dissolution products ($M^+ + H_2O = M OH + H^+$) gives rise to local hydrogenation in pits or (propagating) crack tips. In effect, as the anodic current decreases (less noble potentials) the rate of pitting and subsequent acid hydrolysis decreases giving rise to the maximum observed in Figure 2(A). In the latter, anodic dissolution is necessary for crack propagation to occur (since it leads to acidification) but is not the primary growth mechanism.

While it now seems reasonably well agreed that hydrogen is responsible for failure of high strength steels at both anodic and cathodic potentials in aqueous chloride electrolytes, the matter of crack tip chemistry requires

additional comment particularly in view of the work of Pickering, Frankenthal and co-workers⁴⁰⁻⁴⁴. This interesting work has shown that when a net anodic current flows out of localized geometries (pits, crevices, cracks, etc.) in active metals the potential in the cavity is less noble than at the outer surface, often by more than 1.0 volt. The reverse is true when a cathodic potential is applied to the outer or bulk surface. This potential gradient is understandable in terms of a high resistance path through the electrolyte in the cavity arising from the constriction caused probably by hydrogen bubbles⁴⁰. Hence, the composition (pH, anion and cation concentrations, etc.) as well as potential in a propagating crack may be quite different than that at the bulk electrode surface, and, in consequence, the reactions occurring at the electrode surface and in the crack tip may also be quite different. One may, therefore, expect the possibility of hydrogen evolution from propagating cracks in active metals under anodic polarization, which has been observed in many instances. On the other hand, anodic dissolution may occur at crack tips in cathodically polarized straining electrodes which has also been observed^{42,44}. In effect, both metal dissolution and hydrogen evolution may occur at a crack tip regardless of the electrochemical potentials imposed at the electrode surface. What this means in terms of the potential dependence of the time-to-failure, Figure 2, for example, is that the same mechanism -- whether it be hydrogen embrittlement or APC -- may occur without regard to the applied potential. This is particularly true when pre-cracked specimens are used to monitor crack propagation rates. The mechanism of crack initiation may, with some reservations, be perhaps more meaningfully investigated.

Our general conclusion, and that expressed by Pickering and co-workers as well⁴¹, is that studies of the potential dependence may be mechanistically misleading since under appropriate circumstances both dissolution and hydrogen evolution may occur simultaneously in the crack tip. Hence, evidence of dissolution at a fracture surface need not signal an APC mechanism. Similarly, evolution of hydrogen during propagation does not unequivocally demonstrate that hydrogen embrittlement occurs. The molecular hydrogen which evolves is not troublesome, but, of course, it is the atomic hydrogen which enters the metal that is the cause for concern but only in alloys that are sensitive to hydrogen* -- i.e., in order for hydrogen-induced damage to occur some means must be provided to prevent recombination of atomic hydrogen to form molecular hydrogen. This will be discussed again in a subsequent section. As a case in point, however, we turn our attention next to the question of hydrogen embrittlement in the cracking of austenitic stainless steel in aqueous chlorides.

Shively, et al.⁴⁶ have reported hydrogen permeation through an austenitic stainless steel subject to pitting corrosion (and, hence, pH and potentials different than that at the free surface) in a room temperature chloride solution. In non-pitting environments -- e.g., H₂SO₄ -- no hydrogen permeation was detected at anodic potentials, Figure 3. Since pitting occurs as well in boiling MgCl₂ (150°C), these authors suggest that absorbed hydrogen leads to embrittlement. Hydrogen evolution has been observed from cracks in type 304 stainless steel in boiling MgCl₂⁹. Wilde and Kim¹⁰, however, examined the implication that the production of molecular hydrogen necessarily leads to atomic hydrogen absorption at elevated temperatures. Their findings are shown in Figures 4 and 5. Figure 4 shows the influence of applied

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*Despite the presence of hydrogen within a metal -- as indicated by permeation measurements -- it does not follow that embrittlement must occur. As a case in point, palladium is readily permeated by hydrogen but is not embrittled⁴⁵.

current on the degree of hydrogen absorption in type 304 stainless steel exposed to LiCl solutions (in one case containing recombination poisons) at 146°C. Corresponding cracking behavior (time-to-failure) is shown in Figure 5. Note that under freely corroding conditions (E_{corr}) more hydrogen is absorbed using the poisoned electrolyte as anticipated but that the time-to-failure is increased -- i.e., the specimens were less susceptible to cracking. Moreover, the general increase in hydrogen absorption in the case of the poisoned electrolyte as a function of current does not lead to increased cracking sensitivity. Some hydrogen is absorbed at anodic potentials due probably to pitting. Notice, however, that despite equivalent amounts of absorbed hydrogen, specimens cathodically charged beyond 10^{-6} A/cm^2 do not fail in 500 hours whereas the corresponding anodically polarized specimens fail in a matter of a few hours. Wilde and Kim¹⁰ therefore conclude that this evidence does not support a hydrogen embrittlement model in the case of austenitic stainless steels exposed to hot chlorides, but rather a crack growth mechanism controlled by anodic dissolution.

It should be mentioned at this stage that despite the (we find) convincing evidence from Wilde and Kim¹⁰ there is still no unanimity of opinion on the role of hydrogen in the mechanism of chloride stress corrosion cracking of austenitic stainless steel. This issue has been discussed at considerable length^{7,48}. While it is true that hydrogen can lead to a loss of ductility (ductile failure) in austenites⁴⁹, it does not necessarily follow that brittle transgranular cracks observed when similar steels are exposed to chlorides involves hydrogen. In short, hydrogen-induced reduction in ductility and brittle stress corrosion cracking may well be separate phenomena. Cathodically charged hydrogen does, however, lead to very intense intergranular and transgranular surface cracking on austenitic stainless steel including stable austenitic stainless steel such as type 310 even in the absence of applied stresses⁵⁰⁻⁵⁴. Hence, this form of embrittlement, takes on especially important consequences as the thickness of the specimen decreases. Figure 6 shows typical surface morphology (a) with stress applied and (b) with no external stress applied to type 310 stainless steel cathodically charged in 1 N H_2SO_4 . Transgranular cracks are parallel to slip traces, Figure 6(c).

While Figure 6 refers to non-chloride solutions, some authors^{48,53} have suggested that cracking in chlorides may also involve hydrogen, perhaps by virtue of the formation of hydrogen-induced martensite platelets which serve as preferential paths for crack propagation. Cathodic charging of even stable austenitic stainless steel leads to partial transformation of the fcc austenite to martensitic phases, α' (bcc) and ϵ (hcp)^{48,51,52,54}. It seems not unlikely that lattice strain induced by charging may well account for the surface cracking described above, particularly in Figure 6(b). The depth of damage would be a function of the distance of diffusion of hydrogen into the austenitic lattice. Since the diffusion coefficient at 25°C of hydrogen in fcc metals is very low ($10^{-11} - 10^{-12} \text{ cm}^2/\text{sec}$), only shallow surface cracking is anticipated. That a similar mechanism could account for the transgranular stress corrosion cracking of thick sections in chlorides seems less likely even at 150°C, particularly in view of the observations of Wilde and Kim that no hydrogen absorption occurs under conditions that produce SCC in boiling chlorides, Figures 4 and 5.

The role of hydrogen in cracking of high strength aluminum alloys has been of considerable recent interest and controversy. Until relatively recently hydrogen was not considered likely to be involved in the environmental embrittlement of alloys such as 7075. Indeed, emphasis was placed, for example, on preferential dissolution of constituents in the grain boundary precipitate free zones. (See reference 3 for review). Moreover, the beneficial influence of cathodic polarization on the resistance of aluminum alloys was considered evidence that hydrogen embrittlement could not have been involved. As pointed out by Speidel^{4,55}, however, the latter criterion seems to

be no longer useful. Figure 7 shows the potential dependence of the rate of permeation of hydrogen through aluminum alloy membranes⁵⁶ as well as the crack growth rates in similar alloys taken from several studies^{3,4,55,57}. Notice that crack velocity initially decreases as potentials are made more cathodic -- i.e., as expected if cathodic protection were occurring -- but then increases at even more active potentials. The open circuit potential for alloy 7075-T651 is in the range of -700 to -800 mV, SCE. Interestingly, hydrogen permeation rates in this instance closely parallel the crack growth rates. Hence, there is in this instance a seemingly clear correlation between the ability of hydrogen to permeate the alloy and its cracking susceptibility which suggests that hydrogen may implicitly serve as an embrittling species.

The presence of hydrogen within the lattice, as suggested in Figure 7, does not however establish that hydrogen-induced embrittlement occurs although it is certainly a likely possibility. As pointed out by Speidel⁵⁵, dissolution is still a viable alternative by virtue of the generation of free caustic at cathodic potentials and consequent alkaline attack in aluminum alloys. Recent work in our laboratory⁵⁸ examined some aspects of this issue. In these experiments we found that pre-charging 7075-T6 specimens for 24 hours in aqueous NaCl or Na₂SO₄ solutions led to considerable loss of ductility whereas pre-charging in H₂SO₄ had no apparent effect on mechanical behavior. The increase alkalinity which occurred during pre-charging in neutral solutions led to intense general dissolution of the surface. By contrast, pre-charging in H₂SO₄ led to no significant surface attack. We conclude that the embrittlement which occurred may best be understood in terms of the destabilization of otherwise protective films on the alloy surface (which, in turn, allows hydrogen to enter the lattice) rather than by virtue of crack propagation by a dissolution mechanism. In short, Al₂O₃ films if present prevent access of cathodically produced hydrogen to the metal substrate. As shown in Figure 8(a), the increase alkalinity which arises in initially neutral solutions during cathodic polarization may effectively destabilize the surface Al₂O₃ films exposing bare surfaces which are thereby accessible to cathodic hydrogen. By way of contrast, the alkalinity increase which occurs during pre-charging in H₂SO₄, Figure 8(b), effectively stabilizes Al₂O₃ making hydrogen entry into the substrate more improbable. Hydrogen-induced embrittlement is therefore more likely in the case illustrated in Figure 8(a) but less likely in 8(b).

One may conclude on the basis of the above that Cl⁻ is not an entirely necessary element of the embrittlement sequence. Cl⁻ and other halides are known to accelerate local attack on otherwise protected aluminum alloys. One might therefore consider that these species may in such instances locally disrupt the protective film, again allowing hydrogen access to the metal. In effect, the action of such halides may serve the same net function as increased alkalinity -- i.e., to destabilize the otherwise protective film.

While there is increasing evidence that hydrogen may well play a role in the (aqueous) environment-sensitive fracture of high strength aluminum alloys, one should keep in perspective that this is apparently not a universal characteristic of aluminum alloys. There is little, if any, evidence for example that Al-Cu are sensitive to hydrogen. Moreover, as shall be shown in the next section, there are other indications that both dissolution and hydrogen mechanisms may be involved in the failure of an alloy such as 7075.

3.2. Loading Mode as a Diagnostic Tool

Several recent studies⁵⁹⁻⁶² have shown that the susceptibility of various alloys to environmentally-induced embrittlement is a function of the loading mode. In particular certain alloys which are considered prone to hydrogen-induced embrittlement have been shown to be more susceptible to cracking in aqueous environments when loaded in tension (mode I) than when loaded in torsion (mode III). The work of Green, Hayden and Montague⁵⁹ is notable in this context. They suggest that the decreased susceptibility under torsional loading may be understood in terms of a hydrogen-embrittlement mechanism: under torsional loading the hydrostatic component of stress is not available to drive hydrogen into the region ahead of the crack tip and, hence, cracking in such cases cannot be due to hydrogen. A hydrogen-sensitive alloy is expected therefore to be resistant to environmentally-induced premature failure if loaded in torsion. Conversely, if film rupture or stress accelerated dissolution is a failure mechanism then failure should occur in both tension and torsion since in both instances stressed material is exposed to the environment.

Green et al.⁵⁹ have examined the above views for the case of Ti-8Al-1Mo-1V in aqueous chloride, α -brass in ammoniacal environments, and aluminum alloy 7075-T6 in saline solutions. Their results for the Ti-alloy are shown in Figure 9 as a function of the fracture toughness in air. Under torsional loading the fracture toughness K_{III} , is virtually unaffected by exposure to the environment which in some cases contained hydrogen absorption catalysts such as arsenic. In tension, however, substantial loss of fracture toughness occurs. This observation is consistent with the generally-accepted view that the Ti-alloy is embrittled by hydrogen. For the case of α -brass/ammonia, in which hydrogen is not considered directly involved in failure (rather, a dissolution mechanism is thought to be more likely), the expected sensitivity to both loading modes is observed, Figure 10. It appears, therefore, that the influence of loading mode may be a useful means of distinguishing hydrogen embrittlement from dissolution (SCC) related failure processes.

On this basis the results shown in Figure 11 for the aluminum alloy in saline solutions indicate dissolution as well as hydrogen related components to the failure mechanism. This alloy is strikingly sensitive to the environment when loaded in tension (indicating the importance of hydrogen) and less, but perceptibly, sensitive when loaded in torsion (indicating a dissolution component as well). Note in addition that arsenic when added to the electrolyte accelerates cracking in tension but inhibits failure in torsion. In short, Green et al.⁵⁹ conclude that the predominant mechanism of failure in 7075-T6 involves some form of hydrogen embrittlement, a view consistent with the observations mentioned in an earlier section.

3.3. Importance of Solid State Impurities

The potential importance of impurity segregation at internal interfaces, particularly grain boundaries, in the phenomenology of various forms of embrittlement -- temper embrittlement⁶³, stress corrosion cracking⁶⁴, etc., -- had been proposed some time ago. More recently, surface analytical tools, such as Auger electron spectroscopy have made it possible to substantiate such proposals. For example, temper embrittlement of steels appears related to the grain boundary accumulation of alloying elements such as Ni and Cr and impurity elements (metalloids) such as P, Sb, Sn, etc.⁶⁵⁻⁶⁸ Intergranular embrittlement of W⁶⁹, Cu⁷⁰ and phosphor bronze⁷¹ have been associated with segregated P, Bi, and P, respectively. In many cases embrittlement has been attributed to a reduction in (grain boundary) surface energy, a consequence

of the segregation of solutes to the grain boundary, or to galvanic effects in electrolytes arising out of chemical inhomogeneity between grain boundaries and contiguous grains⁶⁴.

Impurities may also play an important role in hydrogen embrittlement, particularly if the segregated species happen to be metalloids such as those mentioned above which are known to be effective catalytic poisons for the hydrogen recombination reaction in electrolytes. The significance of recombination poisons was first pointed out by Latanision and Opperhauser⁷²⁻⁷⁵ in a study of the intergranular embrittlement of nickel by cathodically produced hydrogen. In particular Sn and Sb were found accumulated on the intergranular fracture surfaces. In essence, it was argued⁷²⁻⁷⁵ that the entry of hydrogen into the nickel occurred preferentially in the proximity of the grain boundary intersections with the free surface due to the presence therein of Sn and Sb (and the absence of Cu) which act to poison the combination of hydrogen atoms formed by the discharge of protons from the electrolyte. At locations remote from the grain boundary, protons are reduced forming hydrogen adatoms which in the absence of a poison have a high probability of combining to form molecular hydrogen and are, thus, subsequently evolved. In the vicinity of a grain boundary, in contrast, rather than evolving from the electrode surface in molecular form, uncombined hydrogen adatoms increase in number at the interface and the probability of their absorption into the metal lattice increases. This is illustrated in Figure 12. It should be noted that the observed absence of copper, which would otherwise stimulate the combination reaction, further increases the probability of atomic hydrogen absorption. Hence one must consider the influence of species which are deficient as well as in excess (relative to the unembrittled condition) on the grain boundaries.

Some of the elements which may be involved in the embrittlement process are shown in the sequence in Figure 13. Recent studies (see reference 76 for a review) suggest that yielding begins in the surface grains of polycrystals through the action of dislocation sources near the free surface. The result is that some hydrogen is dragged into the interior along with mobile dislocations which may then interact with grain boundaries, Figures 13(a) and (b). There is, of course, a finite probability that some hydrogen enters the solid at other than poisoned grain boundaries, evidence for which is the fact serrated yielding has been observed in large-grained polycrystals and in similar experiments with monocrystals^{75,77}. Likewise, atomic hydrogen which enters the solid preferentially at grain boundary intersections with the free surface is likely to diffuse via the grain boundaries into the solid. In the later stages of deformation, internal dislocation sources become operational and the incidence of dislocation interactions with the grain boundaries increases. The attendant stress concentration and the presence of hydrogen in the vicinity of the grain boundaries may then lead to embrittlement, Figure 13(c), perhaps as a result of the chemisorption-induced reduction in the cohesive strength of atomic bonds at regions of stress concentration.

It should be appreciated that the embrittlement of nickel described above is not the result of segregation of Sn and Sb alone as indicated by the fact that identical tensile specimens deformed in the absence of hydrogen were not embrittled. Indeed embrittlement is associated with the interaction between segregated species and the surrounding environment. Such impurity-microchemistry interactions may apply to other metals and alloys as well. For example, it has been observed that the tempering temperature range producing shortest life in steels exposed to cathodic hydrogen corresponds also to the typical temper embrittlement range^{67,78}. Moreover, it is known, as pointed out earlier, that temper embrittlement is associated with grain boundary accumulation of Sb, P, Sn, etc., all of which are very effective hydrogen

recombination poisons. Recognizing that water and water vapor are severely damaging to steels⁷⁹ -- presumably due to the presence of hydrogen produced as the cathodic equivalent of the oxidation or corrosion of iron -- it is tempting to suggest⁷⁵ that temper embrittlement may be due not solely to the accumulation of impurities at the grain boundaries but, as in the case of nickel, in part as well to the local rate of absorption of hydrogen by the matrix. A test of this hypothesis would be to vacuum heat treat a susceptible steel in the temper embrittlement range and, after carefully avoiding exposure to moisture, (i.e., a source of hydrogen), to deform the specimen in a vacuum. It should be mentioned that Yoshino and McMahon⁶⁷ attribute the increased hydrogen sensitivity of temper embrittled steels to the combined effects of impurities and hydrogen in reducing the intergranular cohesive strength. The point of the present discussion is to suggest that the accumulated impurities may be responsible as well for the presence of hydrogen in the grain boundaries.

While we have discussed the importance of impurities largely from the point of view of their influence on hydrogen embrittlement, it might be well to notice that those impurities which increase the rate of hydrogen absorption from electrolytes (i.e., metalloids such as Sn, Sb, S, P, As, etc.) have the concurrent effect of reducing the corrosion rate. Such elements have typically low exchange current densities for the hydrogen evolution reaction. Hence, one expects that in acid or deaerated electrolytes the corrosion rate will be decreased in those regions where the segregation of such metalloids occurs. In effect, in alloys that are not sensitive to hydrogen, susceptibility to cracking, presuming that cracking occurs by a dissolution related mechanism, may be reduced. Preferential selective segregation may therefore provide a means of stress corrosion cracking control.

In a similar context, control of susceptibility in alloys sensitive to cracking during cathodic charging requires quite different control. One would in this case hope to decrease the concentration of metalloids at grain boundaries by, for example, reducing grain size, purification of the alloy, or by providing alternate and non-continuous interfaces as opposed to grain boundaries at which solutes might accumulate. Conversely, while metalloids would have the effect of increasing the rate of atomic hydrogen absorption, noble elements such as Cu, Ag, Pt, Au, etc., would have the opposite influence with regard to cathodic charging. Hence, preferential segregation of noble metals to the grain boundaries of alloys typically embrittled intergranularly during cathodic charging may be beneficial. Somewhat different but related considerations apply if the source of hydrogen is molecular as has been discussed by Berkowitz et al.⁸⁰ In this case, some noble metals (hydrogen dissociation catalysts) segregated to the grain boundaries may stimulate hydrogen absorption and subsequent cracking. On the other hand, catalytic poisons should retard cracking as shown in the interesting work of Liu et al.⁸¹ In effect, a temper embrittled steel is therefore expected to be susceptible to embrittlement in the presence of molecular hydrogen since nickel is reportedly found accumulated in the grain boundaries as well as in electrolytes at cathodic potentials since Sb, P, etc. are present as well as grain boundary contaminants.

In short, identification and/or control of the partitioning of solutes--alloying elements as well as metalloid impurities -- may well provide a clue as to the nature of a particular embrittlement phenomenon (i.e., SCC vs. hydrogen embrittlement) as well as suggest means of reducing susceptibility by metallurgical treatment. Of course, we need at this stage to know much more about the details of such segregation phenomena -- how might one treat an alloy to induce selective segregation; what interactions might one expect between segregated solutes; etc.?

4. Concluding Remarks

What we have attempted to do in this review is to consider some of the means by which stress corrosion cracking has been distinguished from hydrogen embrittlement in electrolytes. There may be others which have not been discussed, and we do not pretend that this statement adequately summarizes all of the many points of view which have emerged. Nevertheless, we do consider that the above represents the essence of some major issues. It seems clear to us that no completely adequate criteria for making the sought after distinction has yet emerged although progress is being made in terms of such issues as loading mode⁵⁹, fractography⁸², etc.

It is also clear that despite years of activity we still do not understand on an atomic scale how and what embrittling species (hydrogen atoms, chloride ions, liquid metal atoms, etc.) do to induce decohesion at a crack tip. This remains to be answered by means other than traditional mechanical testing. Detailed studies of the surface structure, electronic structure, and bonding of adsorbed hydrogen, for example, on strained metal surfaces are totally lacking as far as we are aware but are crucial, we believe, to understanding such phenomena.

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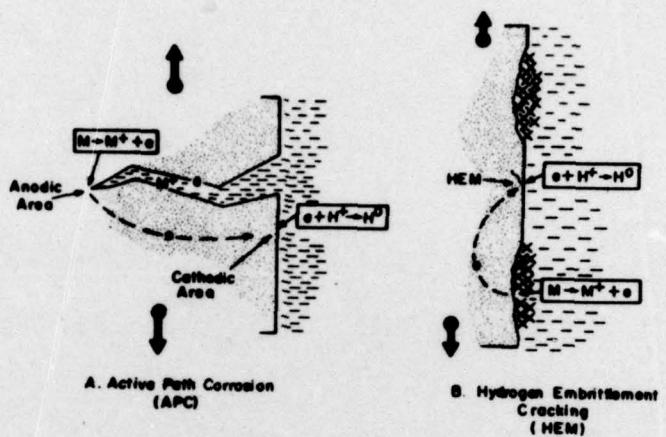
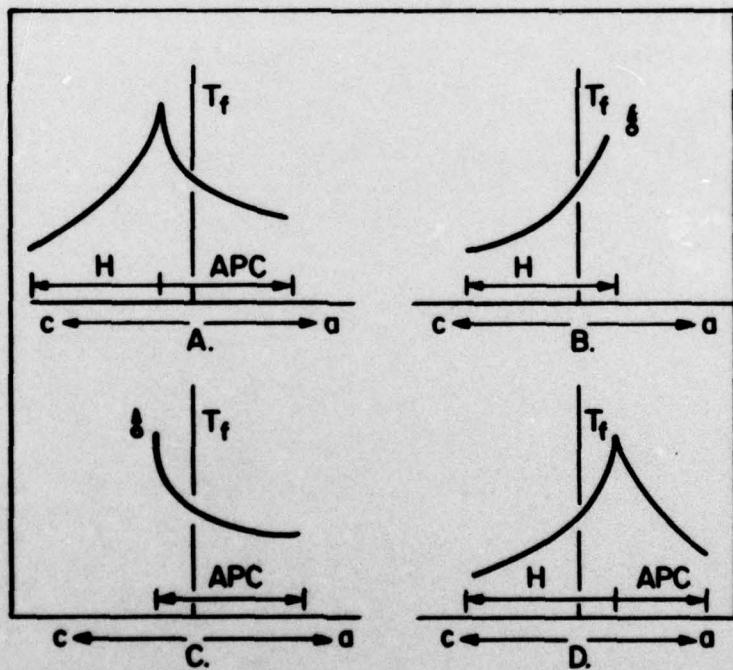


Figure 1. Schematic of cracking by active path corrosion (APC) and hydrogen embrittlement (HEM) mechanisms. (after Wilde³²).



APC Active Path Corrosion c Cathodic Polarization
 T_f Time to Failure H-Hydrogen Embrittlement
 a Anodic Polarization § No Failure

Figure 2. Influence of anodic and cathodic polarization on cracking susceptibility. (after Wilde³²).

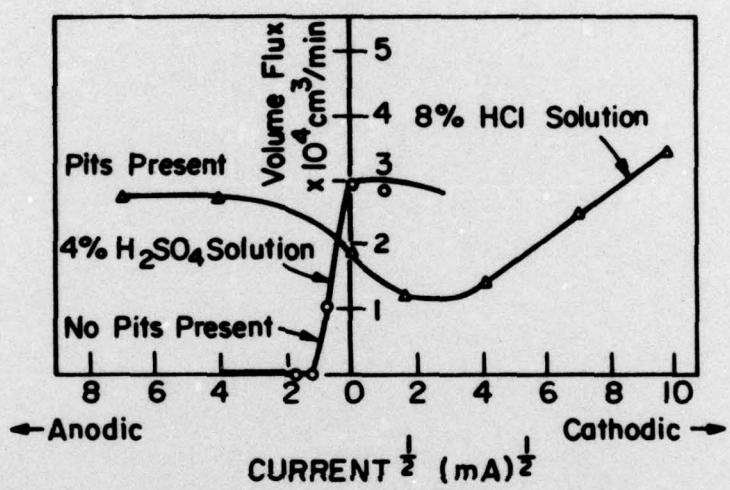


Figure 3. Hydrogen permeation through Type 310 stainless steel as a function of applied current in pitting and non-pitting environments. (from Shively, et al.,⁴⁶; drawing after Payer and Staehle⁴⁷).

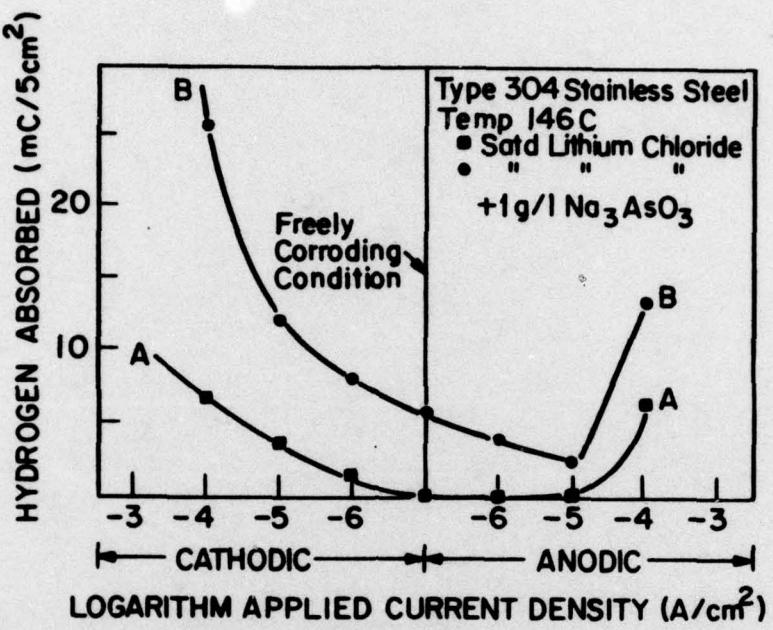


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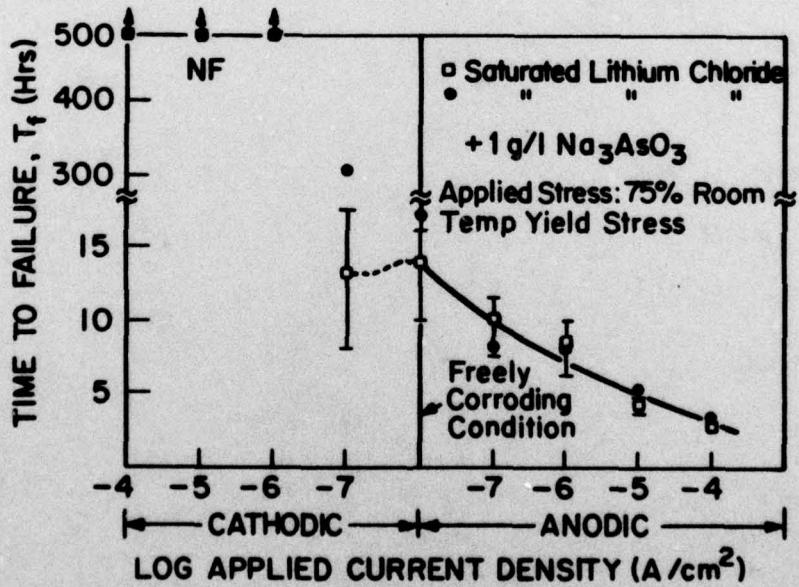


Figure 5. Cracking susceptibility corresponding to Figure 4. (after Wilde and Kim¹⁰).

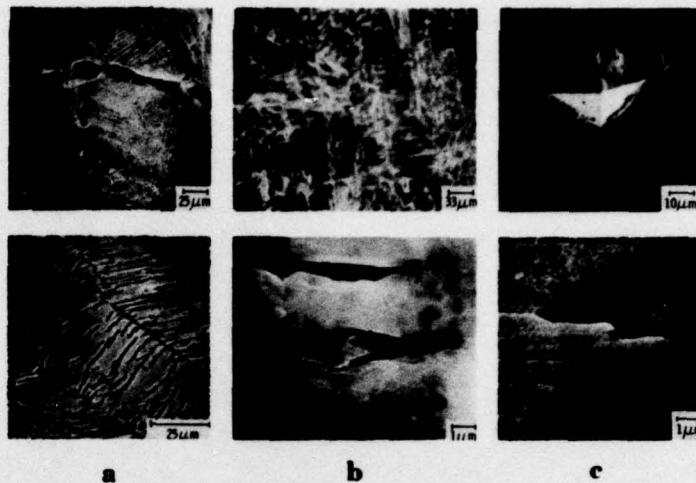


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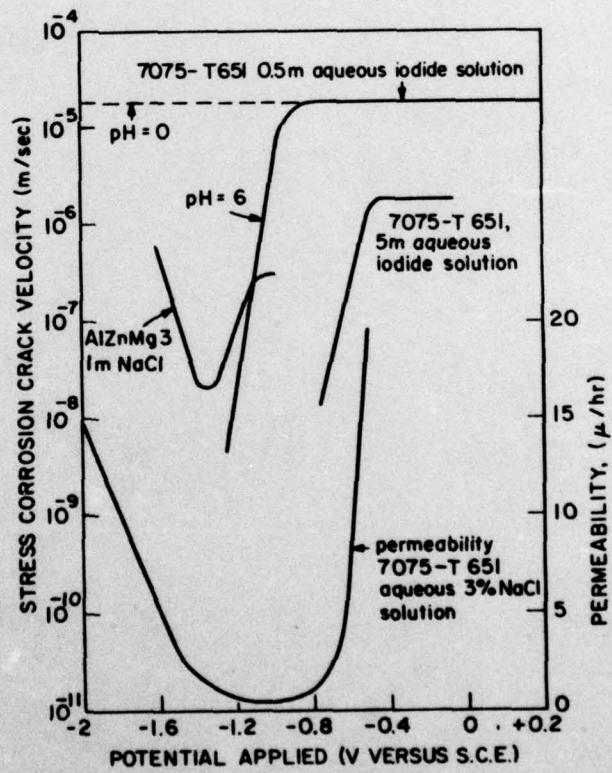


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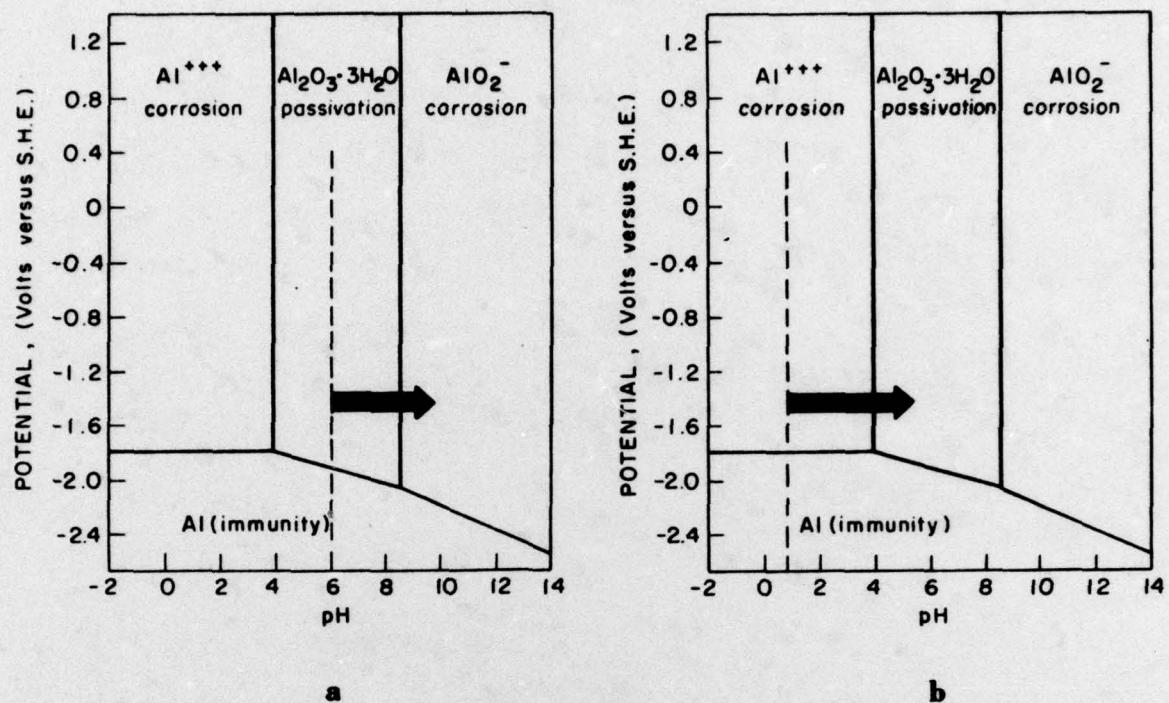


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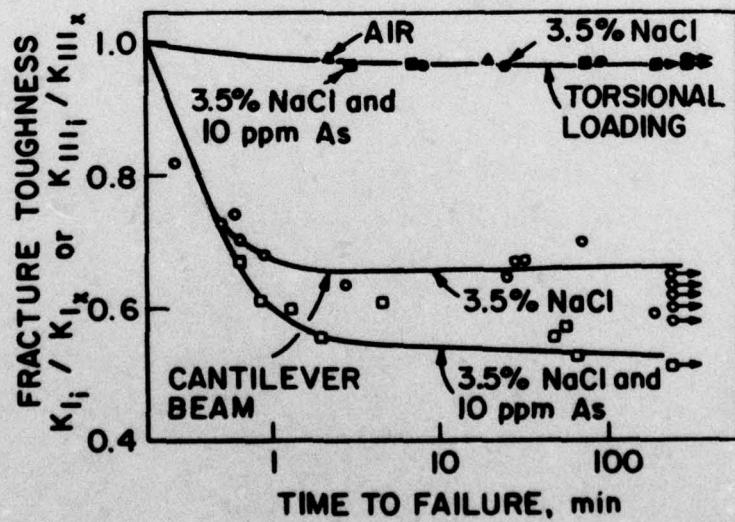


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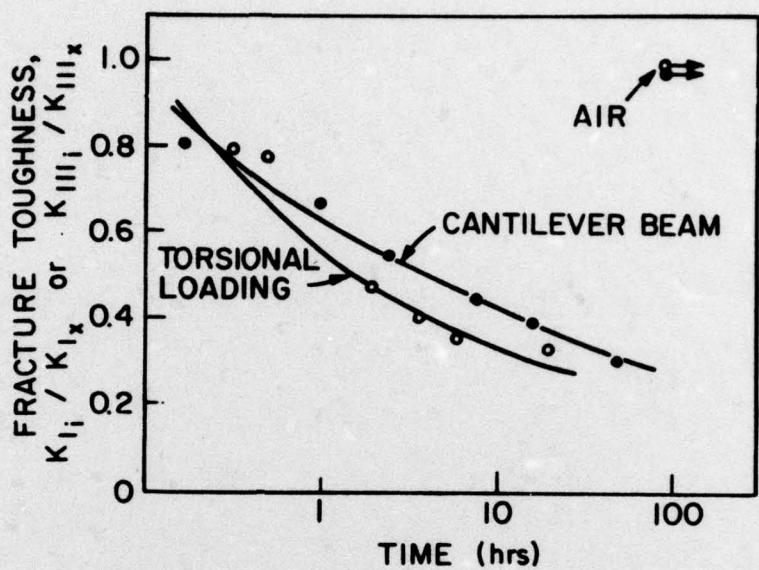


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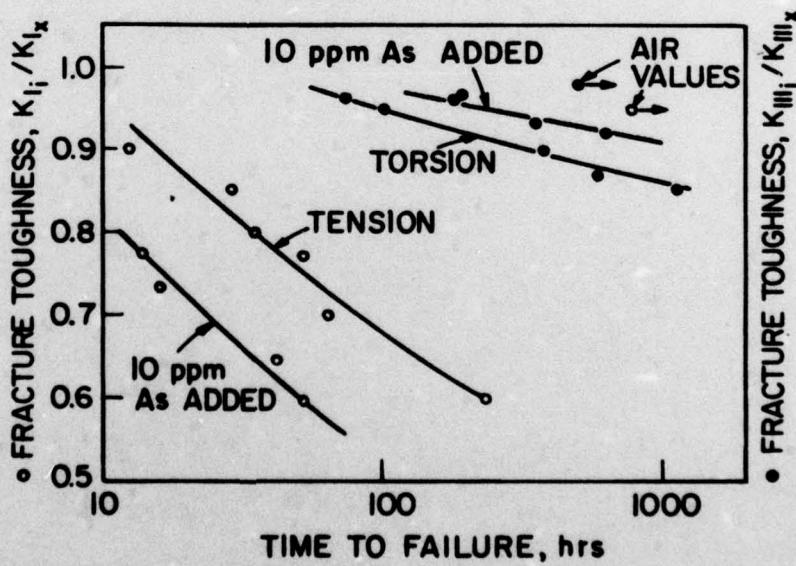


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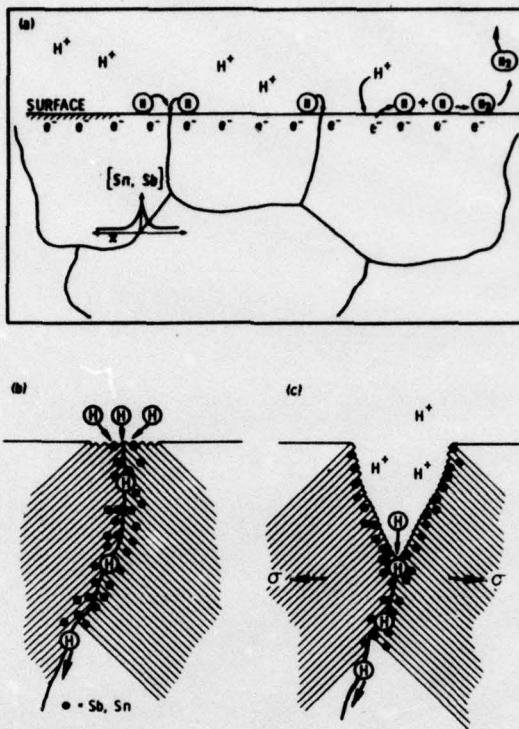


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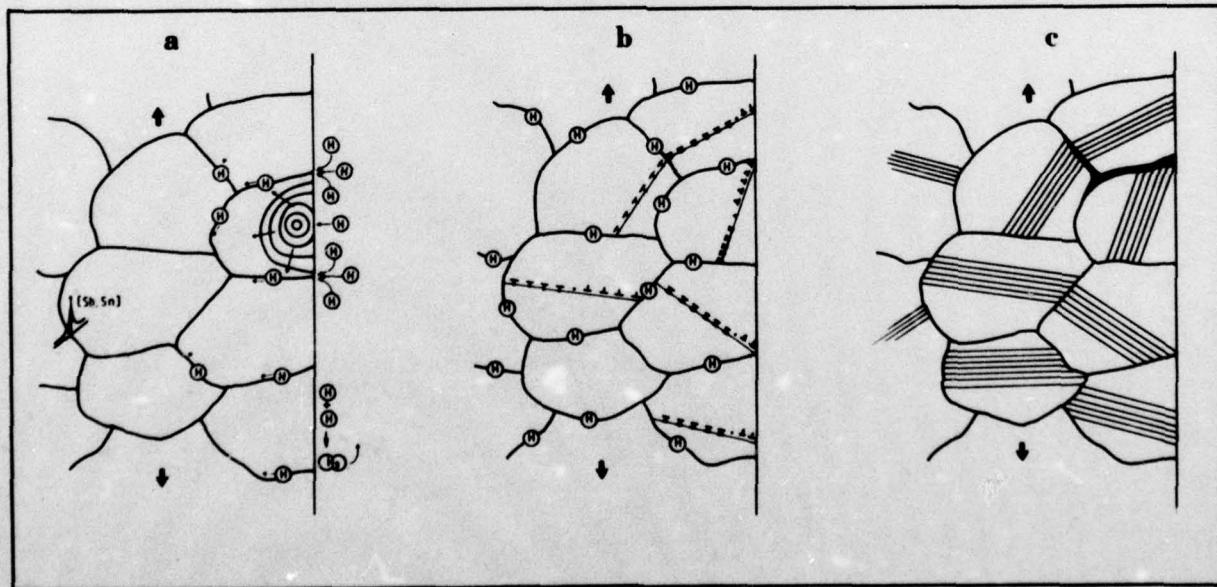


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